
Direct CI Method in Restricted Configuration Spaces

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ABSTRACT

A configuration interaction (CI) method in restricted CI (RCI) space obtained by imposing inequality-type restrictions on the occupancies of groups of molecular orbitals (MOs) was studied. The direct CI approach in such space was analyzed, and some recommendations concerning practical implementation of the RCI method are given. The corresponding program has been written in FORTRAN 77 for an IBM 486 DX personal computer and has been used for electronic structure calculations on transition metal complexes using a valence MO basis with the INDO approximation. © 1996 by John Wiley & Sons, Inc.

Introduction

The *ab initio* calculation of electronic structures of large molecules is expensive even at the Hartree-Fock (HF) level. It can scarcely be expected that in the near future more advanced *ab initio* methods accounting for electron correlation will become a working tool for electronic structure investigations of extensive systems (e.g., supramolecules).¹ Therefore, development of multiconfigurational methods based on valence molecular orbitals bases in semiempirical or pseudopotential approximations is useful. In such methods, the desirability of using large configuration spaces is debatable, since we can expect to get at best semiquantative results. In our opinion, for these

methods restricted CI space obtained from full CI (FCI) space by imposing reasonable restrictions on occupancies of selected MO groups²⁻⁵ are more convenient for the following reasons: (1) It is easy to organize automatic generation of basis determinants satisfying given restrictions on occupancies with minimal input information; (2) such RCI spaces are invariant with respect to the S^2 operator; (3) in the process of calculation of the matrix elements of any operators which can be expressed as linear combinations of unitary group generators and their products, the excitations out of the restricted space chosen can be easily handled; and (4) very efficient algorithms developed in ref. 4 can be used after moderate modifications in the RCI case.

In this article we continue our study of RCI space, which began with ref. 5. A brief theoretical background of the RCI approach is given. In addi-

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tion, we discuss the direct CI method in RCI space, and provide necessary computational details. Finally, we provide sample calculations with RCI wave functions.

Theory

Let us consider electronic states of an N -electron system with a fixed z component of spin M_s , and some orthonormal set of n MOs. We divide this set into κ disjoint groups $A_1, A_2, \dots, A_\kappa$ and impose the following restrictions on the occupancies of these groups:

$$\begin{cases} P_t \leq \text{occ}(A_t) \leq Q_t \\ (t = 1, 2, \dots, \kappa) \\ \text{occ}(A_1) + \dots + \text{occ}(A_\kappa) = N \end{cases} \quad (1)$$

Basis determinants (with fixed M_s) satisfying this system constitute a restricted determinant list (rdl). If an Abelian subgroup of the point symmetry group of the system under consideration is selected, then rdl is a union of symmetry adapted lists.

For basis determinants, we used Handy's split representation (R_α, R_β) ,⁶ where R_σ is interpreted either as a subset of an MO index set $\{1, 2, \dots, n\}$ or as a binary code (σ code) of length n . The number (N_σ) of elements (units) in R_σ is constant since, by assumption, N and M_s are fixed.

To use an efficiently split representation for basis determinants, we replace eq. (1) by two systems:

$$\begin{cases} \max\{0, P_t - \min\{Q_t, n_t\}\} \\ \leq \text{occ}_\sigma(A_t) \leq \min\{Q_t, n_t\} \\ (t = 1, 2, \dots, \kappa) \\ \text{occ}_\sigma(A_1) + \dots + \text{occ}_\sigma(A_\kappa) = N_\sigma \\ (\sigma = \alpha, \beta) \end{cases} \quad (2)$$

where σ codes satisfying this system constitute a restricted σ -list (r σ l). More detailed information concerning the properties of σ codes and their generation is contained in our other article.⁵

We found it convenient to specify the lexical order of r σ l. This means that in the first (from the left) bit position where codes differ, the lesser one has 1. An important property of such ordering is its consistency with the generators action

$$i \geq j \quad \text{and} \quad E_{ij}^\sigma R_\sigma \in \text{r}\sigma\text{l} \Rightarrow E_{ij}^\sigma R_\sigma \geq R_\sigma \quad (3)$$

(We do not distinguish codes $+R_\sigma$ and $-R_\sigma$.) Here E_{ij}^σ stands for the σ component of the unitary group generator defined as

$$E_{ij}^\sigma = a_{i\sigma}^+ a_{j\sigma} \quad (\sigma = \alpha, \beta) \quad (4)$$

Now the lexical order on the restricted determinant list may be specified:

$$\begin{aligned} (R'_\alpha, R'_\beta) &> (R_\alpha, R_\beta) \\ \Leftrightarrow &\begin{cases} \text{either } R'_\alpha > R_\alpha \\ \text{or } R'_\alpha = R_\alpha \text{ and } R'_\beta > R_\beta \end{cases} \quad (5) \end{aligned}$$

Note that in the FCI and Restricted Active Space (RAS) methods, codes in σ lists are normally grouped in symmetry blocks. In the case of the restricted σ lists of general type, we found it more convenient to use the lexical order consistent with the generators action. In the general case, we can hardly avoid storing integer arrays containing order numbers of codes R_α and R_β for every determinant $(R_\alpha, R_\beta) \in \text{rdl}$. Therefore, symmetry blocking of σ lists does not seem to be necessary.

For fast matrix element evaluation, we should have an effective means to determine the order number of σ codes $E_{ij}^\sigma R_\sigma$ if it is known for R_σ . Probably the best way to do this is to use tables (functions) of the type

$$\theta_\sigma(E_{ij}^\sigma, [R_\sigma]) = \pm [R_\sigma \setminus j \cup i] \quad (\sigma = \alpha, \beta) \quad (6)$$

where the numbering function $[\dots]$ is defined by

$$[R_\sigma] = \begin{cases} \text{the order number} \\ \text{of } R_\sigma \text{ in r}\sigma\text{l} & \text{if } R_\sigma \in \text{r}\sigma\text{l} \\ 0 & \text{if } R_\sigma = 0 \\ \tau & \text{if } R_\sigma \in \text{f}\sigma\text{l} \setminus \text{r}\sigma\text{l} \end{cases} \quad (7)$$

Here τ is some special symbol used as a pointer to indicate that σ code has $R_\sigma \neq 0$ and lies outside of r σ l.

In ref. 5, it was proved that knowledge of tables [eq. (6)] is sufficient for the matrix element evaluation of arbitrary operators, which can be expressed as a linear combination of E_{ij}^σ and $E_{ij}^\sigma E_{kl}^{\sigma'}$ ($\sigma, \sigma' = \alpha, \beta$). Of course, in high-speed algorithms, the active rows of tables [eq. (6)] are to be kept in core memory.

If a split representation for basis determinants is used, then it is convenient to recast the electron Hamiltonian as a sum of four terms:

$$\mathbf{H} = H^o + H^\alpha + H^\beta + H^{\alpha\beta} \quad (8)$$

where

$$H^o = 2 \left[\sum_t g_{tt} + 2 \sum_{t \geq u} \frac{(tt|uu)}{1 + \delta_{tu}} \right] I \quad (9a)$$

$$H^\sigma = \sum_{i,j} \left[g_{ij} + 2 \sum_t (ij|tt) \right] E_{ij}^\sigma + \sum_{ij \geq kl} \frac{(ij|kl)}{1 + \delta_{ij,kl}} E_{ij}^\sigma E_{kl}^\sigma \quad (\sigma = \alpha, \beta) \quad (9b)$$

$$H^{\alpha\beta} = \sum_{i,j,k,l} \frac{(ij|kl)}{1 + \delta_{ij,kl}} E_{ij}^\alpha E_{kl}^\beta \quad (9c)$$

Here we have explicitly separated inactive MOs labeled by indexes t, u , and active ones labeled by i, j, k, l . The auxiliary matrix \mathbf{g} may be expressed as (see ref. 4)

$$g_{pq} = \begin{cases} h_{pq} - \sum_{r < p} (pr|rq) - \frac{(pp|pq)}{1 + \delta_{pq}} & \text{if } p \geq q \\ h_{pq} - \sum_{r < p} (pr|rq) & \text{if } p < q \end{cases} \quad (10)$$

Direct CI Method in Restricted Configuration Space

For large-scale CI calculations, diagonalization schemes that do not require storage of the full CI matrix are used. In such schemes, only the product of the CI matrix by some current vector is calculated. Schemes of this type came into active use in quantum chemistry after Roos⁷ introduced the direct CI method. A thorough analysis of this method may be found in ref. 8. A general procedure of the direct CI type based on an iterative perturbation theory is described in ref. 9. This procedure allows one to truncate the CI vector by eliminating basis states that are outside of the selected restricted determinant list.

At present, the direct CI method is normally exploited, together with Davidson-type diagonalization schemes.^{10,11} We discuss here some algorithms for calculating the vector $\mathbf{H}\Psi$ (σ vector in

the original terminology by Roos⁷), where Ψ is some current CI vector:

$$\Psi = \sum_{(\mathbf{R}_\alpha, \mathbf{R}_\beta)} X_{\mathbf{R}_\alpha \mathbf{R}_\beta} |\mathbf{R}_\alpha \mathbf{R}_\beta\rangle \quad (11)$$

and where the sum goes over the restricted determinant list rdl.

We analyze separately the effect of H^σ ($\sigma = \alpha, \beta$) and $H^{\alpha\beta}$ on Ψ . Since the diagonal of \mathbf{H} is used repeatedly in the Davidson algorithm (for evaluation of $\mathbf{H}\Psi$ and of Newton-Raphson shift vectors), it is reasonable to calculate it only once before calling the Davison routine. Therefore, we can analyze contributions to $\mathbf{H}\Psi$ only from the off-diagonal part of \mathbf{H} .

First, let us note that CI vectors are normally sparse (many coordinates $X_{\mathbf{R}_\alpha \mathbf{R}_\beta}$ are equal to zero or close to zero.) Second, in the Davidson scheme there are steps in which, in our opinion, the precise calculation of $\mathbf{H}\Psi$ is unnecessary (at least at the beginning). Therefore, we found it reasonable to introduce restricted determinant lists of currently active determinants:

$$\text{rdl}_{\varepsilon, \Psi} = \{ (\mathbf{R}_\alpha, \mathbf{R}_\beta) \in \text{rdl} : |X_{\mathbf{R}_\alpha \mathbf{R}_\beta}| > \varepsilon \} \quad (12)$$

where ε is some nonnegative number.

Contributions to $\mathbf{H}\Psi$ from the off-diagonal part of H^α may be written in the form

$$[H^\alpha \Psi]_{\text{off-diag}} = \sum_{\mathbf{R}'_\alpha > \mathbf{R}_\alpha} \sum_{\mathbf{R}_\beta} |\mathbf{R}'_\alpha \mathbf{R}_\beta\rangle F(\mathbf{R}'_\alpha) X_{\mathbf{R}_\alpha \mathbf{R}_\beta} + \sum_{\mathbf{R}'_\alpha > \mathbf{R}_\alpha} \sum_{\mathbf{R}_\beta} |\mathbf{R}_\alpha \mathbf{R}_\beta\rangle F(\mathbf{R}'_\alpha) X_{\mathbf{R}'_\alpha \mathbf{R}_\beta} \quad (13)$$

where in the first term sums go over $\mathbf{R}'_\alpha > \mathbf{R}_\alpha$ and \mathbf{R}_β such that

$$(\mathbf{R}'_\alpha, \mathbf{R}_\beta) \in \text{rdl} \quad \text{and} \quad (\mathbf{R}_\alpha, \mathbf{R}_\beta) \in \text{rdl}_{\varepsilon, \Psi}$$

and in the second term sums go over $\mathbf{R}'_\alpha > \mathbf{R}_\alpha$ and \mathbf{R}_β such that

$$(\mathbf{R}'_\alpha, \mathbf{R}_\beta) \in \text{rdl}_{\varepsilon, \Psi} \quad \text{and} \quad (\mathbf{R}_\alpha, \mathbf{R}_\beta) \in \text{rdl}$$

In this formula

$$F(\mathbf{R}'_\alpha) = \langle \mathbf{R}'_\alpha | H^\alpha | \mathbf{R}_\alpha \rangle \quad (14)$$

if $\varepsilon = 0$, then eq. (13) describes the exact contribution to $\mathbf{H}\Psi$ from the off-diagonal part of H^α .

We have chosen eq. (13) for calculation of the contribution from H^α to $\mathbf{H}\Psi$ in order to use as efficiently as possible the lexical order of $r\sigma l$. Indeed, due to the consistency relation of eq. (3), we are able to separate the cases $E_{ij}^\sigma E_{kl}^\sigma R_\sigma > R_\sigma$. A somewhat tedious analysis results in eight admissible order relationships for indexes i, j, k, l :

- | | |
|---------------------|---------------------|
| (1) $i > j > k > l$ | (5) $i > j > k = l$ |
| (2) $j > i > k > l$ | (6) $i > j = k > l$ |
| (3) $i > k > j > l$ | (7) $i > j = k = l$ |
| (4) $i = j > k > l$ | (8) $i = j = k > l$ |

After simple manipulations, we can rewrite the expression for the "lower triangle part" of H^σ in the form

$$H^\sigma = \sum_{k>l} \left[\tilde{\mathbf{g}}_{kl} + \sum_{i=1}^l \frac{(ki|i)}{1 + \delta_{kl}} + \sum_{i=l+1}^{k-1} (kl|ii) \right] E_{kl}^\sigma + \sum_{k \geq l} \sum_{i > k} \sum_j [(ij|kl) - (il|kj)] E_{ij}^\sigma E_{kl}^\sigma \quad (15)$$

where all of the sums go over the active MO indexes, and the inner sum over j is taken over $j > l$ if $k > l$, and over $j = l + 1$ to $j = i - 1$ if $k = l$. Matrix $\tilde{\mathbf{g}}$ in the formula is equal to the active block of matrix \mathbf{g} from eq. (10), plus all inactive contributions.

Use of eq. (15) essentially enables us to shorten the loops over the active MO indexes k, l, i, j when vector \mathbf{F} [see eq. (14)] is calculated. Much more efficient, however, proved to be the selection of currently active σ codes before starting the calculation of the contributions to $\mathbf{H}\Psi$. Specifically, we call σ code R_σ currently active if there exists (at least one) $R'_\alpha > R_\alpha$ that gives a nonzero contribution to the right-hand side of eq. (13). In more formal language, it means that there exist α -code $R'_\alpha > R_\alpha$ and β -code R_β such that $(R_\alpha, R_\beta) \in \text{rdl}$ and $(R'_\alpha, R_\beta) \in \text{rdl}_{\varepsilon, \Psi}$ or $(R_\alpha, R_\beta) \in \text{rdl}_{\varepsilon, \Psi}$ and $(R'_\alpha, R_\beta) \in \text{rdl}$. Currently active β codes are defined in an analogous manner. To our surprise, in most cases the number of currently active codes appeared to be much less than the full number of codes in $r\sigma l$ (even if $\varepsilon = 0$). We illustrate this in the next section.

Thus, before calling the routine for the calculation of $\mathbf{H}\Psi$, we suggest a simple preliminary analysis. First, we cut the "tail" of Ψ by forming $\text{rdl}_{\varepsilon, \Psi}$. Second, using rdl and $\text{rdl}_{\varepsilon, \Psi}$, we select currently active α and β codes. Then we use the algorithm of eq. (20) from ref. 4 with the following modifications: (1) The outer loop goes over cur-

rently active σ codes; (2) for calculation of vector \mathbf{F} , we use "short" loops over k, l, i, j in accordance with eq. (15) to get components $F(R'_\sigma)$ of \mathbf{F} with $R'_\sigma > R_\sigma$; and (3) we evaluate contribution to $\mathbf{H}\Psi$ using eq. (13).

Now let us turn to the contributions from the mixed operator $H^{\alpha\beta}$. For each pair i, j of an active MO and for each $R_\beta \in r\beta l$, we put

$$Q_{ij} = \sum_{(R'_\alpha, R'_\alpha)} \sum_{R'_\beta} |R'_\alpha R'_\beta\rangle X_{R'_\alpha R'_\beta} \langle R'_\alpha | E_{ij}^\alpha | R_\alpha \rangle \langle R'_\beta |, \quad (16)$$

and

$$F_{ij}(R_\beta) = \sum_{R'_\beta} |R'_\beta\rangle \sum_{k,l} \langle R'_\beta | E_{kl}^\beta | R_\beta \rangle (ij|kl) \quad (17)$$

where in eq. (16) the outer sum goes over pairs (R_α, R'_α) such that $R'_\alpha = \pm E_{ij}^\alpha R_\alpha$, and the inner sum goes over $R'_\beta \in r\beta l$ such that $(R'_\alpha, R'_\beta) \in \text{rdl}_{\varepsilon, \Psi}$. In eq. (17) the outer sum goes over $r\beta l$.

Using these definitions, we can write

$$H^{\alpha\beta} \Psi = \sum_{i,j} \sum_{R_\beta} Q_{ij} * F_{ij}(R_\beta) \quad (18)$$

where $*$ means that after multiplication we should omit all the contributions $X_{R'_\alpha R'_\beta} \langle R'_\alpha | E_{ij}^\alpha | R_\alpha \rangle \langle R'_\beta | E_{kl}^\beta | R_\beta \rangle (ij|kl)$ with $(R_\alpha, R_\beta) \notin \text{rdl}$ [in the FCI case without point symmetry restrictions $\text{rdl} = r\alpha l \times r\beta l$, and in eq. (18) we have the standard bra by ket product].

After experiments with different loop structures, we came to the conclusion that for the "mixed" operator $H^{\alpha\beta}$, attempts to use the lexical order on $r\sigma l$ and on rdl did not lead to a more effective algorithm than algorithm (23) from ref. 4. Therefore, we used the latter with the following modifications: (1) In the outer loop over i, j , we calculate Q_{ij} using the currently active determinant list $\text{rdl}_{\varepsilon, \Psi}$; (2) since in constructing Q_{ij} , only α codes such that $E_{ij}^\alpha R_\alpha \neq 0$, τ are active, we found it efficient to select only those R_β which occur in pairs $(R_\alpha, R_\beta) \in \text{rdl}$ with those R_α involved in Q_{ij} ; and (3) in the loop over R_β , we use only β codes that were selected at stage (2).

In the Davidson scheme,^{10,11} there are two steps in which the product $\mathbf{H}\Psi$ is required. When we calculate $\mathbf{H}\Psi$ to augment the current block of the Hamiltonian, sufficiently high accuracy is necessary. We should therefore use "long" lists $\text{rdl}_{\varepsilon_1, \Psi}$ with small ε_1 . When, on the other hand, we calculate $\mathbf{H}\Psi$ to construct the Newton-Raphson shift vector, the accuracy is not that important (at least

initially), and we can use comparatively short lists $\text{rdl}_{\varepsilon_2, \Psi}$. In our opinion, after initialization of ε_2 , it is reasonable to replace it by, say $\varepsilon_2/2^j$, where j is the number of current Newton-Raphson steps. If $\varepsilon_2/2^j < \varepsilon_1$, then we should put $\varepsilon_2 = \varepsilon_1$.

The described algorithm has been implemented on an IBM 486 DX personal computer. The program has been written in FORTRAN 77, and at present it is attached to an existing set of semiempirical programs designed to calculate the electronic structure of transition metal compounds by the INDO-E method.¹² All of the algorithms are written in such a way that the underlying method for MO generation (semiempirical or *ab initio*) is important only for the evaluation of the $\tilde{\mathbf{g}}$ matrix [see eq. (15)] and for the formation of the active integral list ($ij|kl$). The efficiency of our algorithm for the CI vector calculation does *not* depend on the number of inequalities imposed on the occupancies of the MO groups. In particular, we can use the individual restrictions on the occupancy of each active MO. From Table I one can get an impression of to what extent it is possible to truncate the CI vector by imposing this type of restriction.

In concluding this section, it seems pertinent to mention that we have found the original Davidson algorithm¹⁰ not very reliable. With poor trial vectors, the desired eigenstate may, for example, collapse to the lower one (see also ref. 11). A simple modification of the Davidson algorithm to treat a

group of successive states has proved more reliable. We have used the gravity center of the Davidson shift vectors as a current shift vector:

$$\mathbf{d} = -(H_0 - E_{\text{av}})^{-1} \sum_{m \in S} (HC_m - E_m C_m) \quad (19)$$

where

$$E_{\text{av}} = 1/|S| \sum_{m \in S} E_m \quad (20)$$

The rigorous justification of such an approach is hardly possible, since at each step we use n -parametric shifts (here n is the length of vector \mathbf{d}) to determine finally the set of $|S|$ vectors which is controlled by $n|S| - |S|(|S| + 1)/2$ parameters. Nevertheless, the convergency of the Davidson iterative process with shift vector [eq. (19)] proved to be sufficiently stable, and the core and disc memory requirements are the same as in the original Davidson scheme. In our calculations, we have treated simultaneously up to 20 electronic states.

Sample Calculations

Here we try to illustrate by example the formal reasoning of the previous sections by calculations on the cation $[(\text{NH}_3)_5\text{Ru}-\text{Pyz}]^{3+}$. Symmetry adapted (with respect to C_{2v} point group) valence MOs were generated by solving the *HF* equation

TABLE I.
The Length of the Determinant Expansion of RCI Vector as a Function of the Number of Active MOs with Restrictions $0 \leq \text{occ}(\varphi_i) \leq 2$ for the Case of Eight Electrons Correlated in 13 Active MOs.

Number of Active MOs with Restriction $1 \leq \text{occ}(\varphi_i) \leq 2$	Number of Active MOs with Restrictions $0 \leq \text{occ}(\varphi_i) \leq 2$	Number of Active MOs with Restrictions $0 \leq \text{occ}(\varphi_i) \leq 1$	Number of Basis Determinants
0	13	0	511225
0	12	1	462825
1	11	1	245025
1	10	2	224850
2	9	2	113646
2	8	3	105836
3	7	3	50305
3	6	4	45598
4	5	4	20789
4	4	5	20001
5	3	5	7730
5	2	6	7650
6	1	6	2420

with the INDO-E approximation (see ref. 12) for the closed-shell cation $[(\text{NH}_3)_5\text{Ru}-\text{Pyz}]^{2+}$. MOs ordered in accordance with "Aufbau" principle were divided into 15 groups. These groups and their minimal and maximal occupancies are given in Table II.

After reordering the MOs to collect in the first group all inactive orbitals and in the last group all virtual orbitals, we got 10 groups, of which 8 corresponded to 14 active MOs.

On the basis of the inequalities of Eq. (2) for the case of the spin projection $M_s = 1/2$ and the total number of electrons $N = 75$, 213 α codes and 594 β codes were generated. The full determinant list $r\alpha l \times r\beta l$ contains 162,162 basis determinants, of which we selected 1240 ones satisfying the inequalities of eq. (1) and belonging to irrep A_2 .

First we performed straightforward calculations using the Davidson algorithm with the Hamiltonian lower triangle kept in core memory. Hamiltonian matrix construction took 140 s of CPU time, and each multiplication of H by a trial CI vector required 7 s. Three one-determinant trial vectors corresponding to the three lowest diagonal elements of the Hamiltonian were used. Convergence with respect to the Davidson qnorm parameter was reached in 10 steps (a reasonable for semiempirical calculations qnorm < 0.001 criterion was used).

TABLE II.
Chosen Subdivision of HF MO Set for
 $[(\text{NH}_3)_5\text{Ru}-\text{Pyz}]^{2+}$ and Frontier Occupancies.

Group Number	MO Included in Group	Minimal Occupancy	Maximal Occupancy
1	$\varphi_1 - \varphi_{15}$	30	30
2	φ_{16}	1	2
3	$\varphi_{17} - \varphi_{21}$	10	10
4	φ_{22}	1	2
5	$\varphi_{23} - \varphi_{26}$	8	8
6	$\varphi_{27} - \varphi_{28}$	3	4
7	$\varphi_{29} - \varphi_{30}$	4	4
8	$\varphi_{31} - \varphi_{32}$	3	4
9	$\varphi_{33} - \varphi_{34}$	4	4
10	φ_{35}	1	2
11	$\varphi_{36} - \varphi_{38}$	4	6
12	$\varphi_{39} - \varphi_{40}$	0	1
13	$\varphi_{41} - \varphi_{44}$	0	0
14	$\varphi_{45} - \varphi_{46}$	0	1
15	$\varphi_{47} - \varphi_{72}$	0	0

Then we performed the same calculation using the procedure described earlier with $\varepsilon_1 = 0.0001$ and $\varepsilon_2 = 0.01$. Calculation of $H\Phi_i$ ($i = 1, 2, 3$), where Φ_i is the initial one-determinant vector took 16 s of CPU time. The largest restricted determinant list included 350 active determinants (on the Davidson step number 8). On this step 173 α codes and 252 β codes were active. Calculation of $H\Psi$ required 31 s of CPU time.

It could be expected that for $\varepsilon_1 = \varepsilon_2 = 0$, the time per iteration should be approximately equal to the Hamiltonian construction time plus multiplication of H by Ψ time—that is, about 150 s. However, in spite of the fact that on each iteration 1240 determinants were active, the numbers of active α codes and β codes were equal to 207 and 278, respectively, which reduced the required CPU time per iteration to 50 s. The reason for this lies in the explicit use of the sparseness of $r\alpha l$ (due to symmetry and occupation restrictions) compared to $r\alpha l \times r\beta l$. Note in conclusion that all the timings given are of a relative character, since for personal computers, there is a strong dependence of timings on the PC configuration.

Conclusion

We have studied a version of the direct CI method in configurational space obtained from an FCI space by imposing inequality-type restrictions on the orbital occupancies. To speed up the direct CI iterations, we have found it useful to perform a simple preliminary analysis of the current vector Ψ to construct currently active lists of determinants and σ codes before calculation of the $H\Psi$ vector. Such an approach essentially reduces the required CPU time per Davidson iteration.

The corresponding algorithms have been developed and implemented on an IBM 486 DX personal computer. The program has been carefully tested on the semiempirical (INDO) level and has proved to be rather efficient for treating large molecules involving transition metals. In particular, the nature of metal-metal interactions in the systems with "quadrupole" bonds $[M_2(\text{OOCH}_3)_4] \cdot 2\text{H}_2\text{O}$ ($M = \text{Cr}, \text{Mo}$) was studied, and the exchange parameters for these complexes were calculated.^{13,14} On the base of this program, we have begun a systematic investigation of mono- and binuclear transition metal complexes. This work is currently in progress.

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